

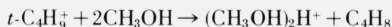
Kinetic Mass Spectrometric Investigation of the Reactions of $t\text{-C}_4\text{H}_9^+$ Ions With Some Simple Polar Molecules at Thermal Energies*

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The interactions of $t\text{-C}_4\text{H}_9^+$ ions from neopentane with some simple polar molecules have been investigated in a high pressure photoionization mass spectrometer at thermal kinetic energies. Proton transfer was found to occur from $t\text{-C}_4\text{H}_9^+$ to acetone, ammonia, and the various methylamines, but not to molecules having estimated proton affinities < 195 kcal/mol (815 kJ/mol). Macroscopic thermal rate coefficients are reported for the various proton transfer reactions, all of which are on the order of 10^{-9} cm³/molecule · second. The reaction



was found to occur, but not the analogous reaction with H_2O . On the basis of supplementary experiments, new limits are reported for the proton affinity of acetone. These are 203 ± 2 kcal/mol $<$ proton affinity of acetone < 207 kcal/mol.

Key words: Ion molecule reactions; mass spectrometry; neopentane; photoionization; proton affinity; rate constants.

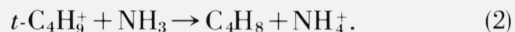
1. Introduction

In a recent article from this laboratory [1]¹ the relative rates of chemical reaction of $t\text{-C}_4\text{H}_9^+$ ions with a variety of hydrocarbons were reported. The method involved the radiolysis of neopentane, which yields $t\text{-C}_4\text{H}_9^+$ as the major fragment ion, carried out in the presence of small quantities of mixtures of deuterated and nondeuterated hydrocarbons (RH_2). The specific reaction investigated was the hydride transfer process



which was monitored by determining the isotopic composition and yield of the stable chemical end-product, isobutane. Although the relative reactivities of some 22 $\text{C}_5\text{-C}_8$ alkanes were determined with a high precision by this method, absolute rate coefficients for Process (1) could only be estimated by assuming the maximum theoretical value (4.0×10^{-9} cm³/mole-

cule · second) for the proton transfer reaction involving $t\text{-C}_4\text{H}_9^+$ and NH_3



The ion-molecule reactions involving $t\text{-C}_4\text{H}_9^+$ ions and certain organic molecules have also been investigated by the techniques of high pressure electron impact mass spectrometry, using both conventional single stage [2] and modified chemical ionization instruments [3, 4]. However, absolute rate constants have been determined and/or estimated for only a relatively few systems.

As part of a continuing program involving ion-chemistry in the vapor phase we have investigated the interactions of $t\text{-C}_4\text{H}_9^+$ with simple polar molecules at thermal kinetic energies in the NBS high pressure photoionization mass spectrometer. Neopentane was chosen as the source of $t\text{-C}_4\text{H}_9^+$ since the photoionization of this molecule at 106.7–104.8 nm (argon resonance lamp) yields only $t\text{-C}_4\text{H}_9^+$ and $i\text{-C}_4\text{H}_8^+$ as fragment ions [5]. It is also known that neopentane is very unreactive towards $t\text{-C}_4\text{H}_9^+$ [1, 5–7]; consequently these ions are available for reaction with any additive compounds chosen for investigation. In pursuing this study we hoped to convert the relative rate constants which were previously measured in this laboratory to an

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¹ Figures in brackets indicate the literature references at the end of this paper.

absolute basis, as well as provide information concerning the overall reactivity of $t\text{-C}_4\text{H}_9^+$ and, perhaps, the proton affinities of some simple polar molecules in the vapor phase.

2. Experimental and Results

All experiments were carried out at 298 K with the NBS high pressure photoionization mass spectrometer described in detail elsewhere [8, 9]. API neopentane was used without further purification. The additive compounds, which were of research grade quality obtained from various sources, were also used without further purification except for outgassing and fractional distillation in vacuo.

2.1. Photoionization of Neopentane at 116.5 and 106.7–104.8 nm

Results obtained from the photoionization of pure neopentane (ionization threshold = 10.37 eV [10], 128.2 nm) at 116.5 and 106.7–104.8 nm are displayed in figure 1. In agreement with previous electron impact and photoionization results parent ions from neopentane were not detected at any wavelength. At 116.5 nm (Kr resonance lamp) the primary mass spectrum consists of 42.5 percent C_4H_8^+ and 57.5 percent $t\text{-C}_4\text{H}_9^+$. At 106.7–104.8 nm (argon resonance lamp), where the majority of the experiments were carried out, photoionization of neopentane yields 89 percent $t\text{-C}_4\text{H}_9^+$ and 11 percent C_4H_8^+ . No additional ions were detected at any wavelength at pressures up to approximately 1 torr, and the $\text{C}_4\text{H}_8^+/\text{C}_4\text{H}_9^+$ ratio remained constant over this range. This behavior indicates an upper limit for the bimolecular rate constant for reaction of C_4H_8^+ and C_4H_9^+ with neopentane of 10^{-14} $\text{cm}^3/\text{molecule} \cdot \text{second}$ at 298 K, which is consistent with the conclusions of earlier mass spectrometric [7, 11] and radiolysis studies [1, 6].

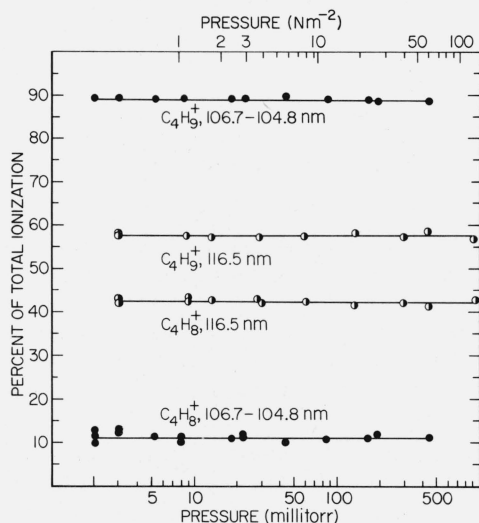
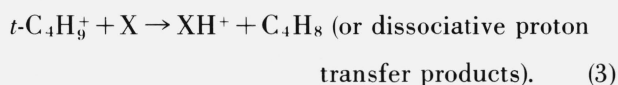


FIGURE 1. Photoionization of neopentane at 116.5 nm and 106.7–104.8 nm as a function of chamber pressure.

2.2. Photoionization of Neopentane in the Presence of Polar Additives

Neopentane was photolyzed in the presence of varying amounts of H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{CHOH}$, CH_3CHO , CH_3COCH_3 , CH_3OCH_3 , NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ at 106.7–104.8 nm. A systematic search was made in each neopentane-additive combination for a bimolecular chemical reaction involving $t\text{-C}_4\text{H}_9^+$ and the polar component (X) in the mixture, particularly the unimolecular decomposition process involving the collision complex which is equivalent to proton transfer:

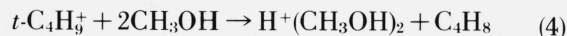


The compositions of the mixtures were generally varied from 3 to 90 percent neopentane. No reactions involving neutral neopentane and the ionized polar component in the mixtures were detected. The results of the various experiments are summarized in table 1, which is arranged in the order of increasing proton affinity (P.A.) of the polar additive. Absolute values for the P.A.'s of the additives are also included, insofar as they are known, except in those cases where only the relative basicities have been established (as in the amines).

The following comments may be made concerning the specific behavior found for the various reaction pairs:

(a) Water—Due to the higher ionization potential of H_2O (I.P. = 12.6 eV [17]) the photolysis of neopentane- H_2O mixtures at 106.7–104.8 nm resulted in a primary mass spectrum containing only C_4H_8^+ and $t\text{-C}_4\text{H}_9^+$. Process 3 was not detected in any experiment. The termolecular reaction $t\text{-C}_4\text{H}_9^+ + 2\text{H}_2\text{O} \rightarrow \text{H}^+(\text{H}_2\text{O})_2 + \text{C}_4\text{H}_8$ involving two water molecules was also not found to occur in mixtures containing as much as 97 percent H_2O . The only process detected was the formation of the stabilized $t\text{-C}_4\text{H}_9^+ \cdot \text{H}_2\text{O}$ adduct at pressures in excess of 20 to 30 millitorr, presumably via a termolecular association reaction. The rate constant for this extremely inefficient process was not estimated.

(b) Methanol—The photoionization of neopentane- CH_3OH mixtures was carried out at 116.5 nm (10.6 eV) since primary ionization of CH_3OH (I.P. CH_3OH = 10.85 eV) does not occur at this wavelength. No bimolecular reactions involving $t\text{-C}_4\text{H}_9^+$ and CH_3OH were detected. However, the extremely efficient termolecular process



was observed in all experiments. A rate coefficient of $3.6 \pm 1.5 \times 10^{-26}$ $\text{cm}^6/\text{molecule}^2 \cdot \text{second}$ was derived for this process using the techniques described in an earlier article [12c].

(c) Acetaldehyde—Although Process 3 was not detected, a slow bimolecular addition reaction



TABLE 1. Reactions of $t\text{-C}_4\text{H}_9^+$ with some polar molecules at 298 K $t\text{-C}_4\text{H}_9^+ + \text{X} \rightarrow \text{products}$ ^a

X	P. A. (X) ^b	Reaction found
H ₂ O	163 ± 5 ^c (681 ± 21)	$t\text{-C}_4\text{H}_9^+ + \text{H}_2\text{O} \xrightarrow{\text{M}} \text{C}_4\text{H}_9\text{H}_2\text{O}^+ + \text{M}$
CH ₃ OH	182 ± 3 ^d (761 ± 13)	$t\text{-C}_4\text{H}_9^+ + 2\text{CH}_3\text{OH} \rightarrow \text{H}^+(\text{CH}_3\text{OH})_2 + \text{C}_4\text{H}_8$
CH ₃ CHO	183 ± 2 ^e (765 ± 8)	$t\text{-C}_4\text{H}_9^+ + \text{CH}_3\text{CHO} \Rightarrow \text{C}_4\text{H}_9\text{CH}_3\text{CHO}^+$
C ₂ H ₅ OH	187 ± 2 ^d (782 ± 8)	No bimolecular reaction
CH ₃ OCH ₃	191 ± 10 ^f (798 ± 40)	$t\text{-C}_4\text{H}_9^+ + \text{CH}_3\text{OCH}_3 \xrightarrow{\text{M}} \text{C}_4\text{H}_9\text{CH}_3\text{OCH}_3^+ + \text{M}$
<i>i</i> -C ₃ H ₇ OH	193 ± 5 ^e (807 ± 21)	$t\text{-C}_4\text{H}_9^+ + i\text{-C}_3\text{H}_7\text{OH} \xrightarrow{\text{M}} \text{C}_4\text{H}_9\text{C}_3\text{H}_7\text{OH}^+ + \text{M}$
CH ₃ COCH ₃	≥ 202.6 ^g (847)	$t\text{-C}_4\text{H}_9^+ + \text{CH}_3\text{COCH}_3 \rightarrow (\text{CH}_3\text{COCH}_3)\text{H}^+ + \text{C}_4\text{H}_8$ $k = 1.2 \pm 0.1$; ($k_a = 1.09$, $k_\mu = 5.5$)
NH ₃	207 ^h (865)	$t\text{-C}_4\text{H}_9^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{C}_4\text{H}_8$ $k = 0.90 \pm 0.08$; ($k_a = 0.96$, $k_\mu = 4.2$)
CH ₃ NH ₂	ⁱ > 207	$t\text{-C}_4\text{H}_9^+ + \text{CH}_3\text{NH}_2 \Rightarrow (\text{CH}_3\text{NH}_2)\text{H}^+ + \text{C}_4\text{H}_8$ $k = 1.3 \pm 0.1$; ($k_a = 1.2$, $k_\mu = 3.0$)
(CH ₃) ₂ NH	ⁱ > CH ₃ NH ₂	$t\text{-C}_4\text{H}_9^+ + (\text{CH}_3)_2\text{NH} \Rightarrow (\text{CH}_3)_2\text{NH}_2^+ + \text{C}_4\text{H}_8$ $k = 1.2 \pm 0.05$; ($k_a = 1.2$, $k_\mu = 2.1$)
(CH ₃) ₃ N	ⁱ > (CH ₃) ₂ NH	$t\text{-C}_4\text{H}_9^+ + (\text{CH}_3)_3\text{N} \Rightarrow (\text{CH}_3)_3\text{NH}^+ + \text{C}_4\text{H}_8$ $k = 1.2 \pm 0.1$; ($k_a = 1.25$, $k_\mu = 1.2$)

^a Where rate coefficients are given, the units are cm³/molecule · second × 10⁻⁹.^b First entry, kcal/mol; second entry, kJ/mol.^c Ref. [12].^d Ref. [13].^e Ref. [14].^f Ref. [15].^g See discussion.^h Ref. [12b].ⁱ Order of basicities given in Ref. [16].

was observed. The rate coefficient for this Process was found to be $4.2 \pm 0.5 \times 10^{-11}$ cm³/molecule · second.

(d) Ethanol—No bimolecular reactions were found involving $t\text{-C}_4\text{H}_9^+$ and C₂H₅OH.

(e) Dimethyl ether—No bimolecular reactions were observed, although the formation of the $[\text{C}_4\text{H}_9\text{CH}_3\text{OCH}_3]^+$ adduct was detected at pressures in excess of 15 to 20 millitorr.

(f) Isopropanol—Again no bimolecular reactions were found, although the stabilized adduct $[\text{C}_4\text{H}_9(\text{CH}_3)_2\text{CHOH}]^+$ was detected at pressures in excess of ~20 millitorr.

(g) Acetone—The bimolecular proton transfer process



was found to occur efficiently in neopentane-acetone mixtures. Typical data obtained for the rates of formation and disappearance of the major ions resulting from the photolysis of a 1:1 mixture at 106.7–104.8 nm as a function of chamber pressure are shown in figure 2. At these wavelengths the primary mass spectrum of acetone contains 84 percent $\text{CH}_3\text{COCH}_3^+$ and 16 percent CH_3CO^+ , which accounts for the appearance of CH_3CO^+ in figure 2. Separate experiments involving acetone alone verified that CH_3CO^+ reacts with acetone via proton transfer, while $\text{CH}_3\text{COCH}_3^+$ reacts both by proton transfer and via formation of $(\text{CH}_3\text{COCH}_3)\text{CH}_3\text{CO}^+$. The detailed results pertinent to pure acetone and other ketones will be discussed at a later date.

The macroscopic rate coefficient for Process 6 was derived by the method described [9] previously through consideration of the slope of the decay curve in that

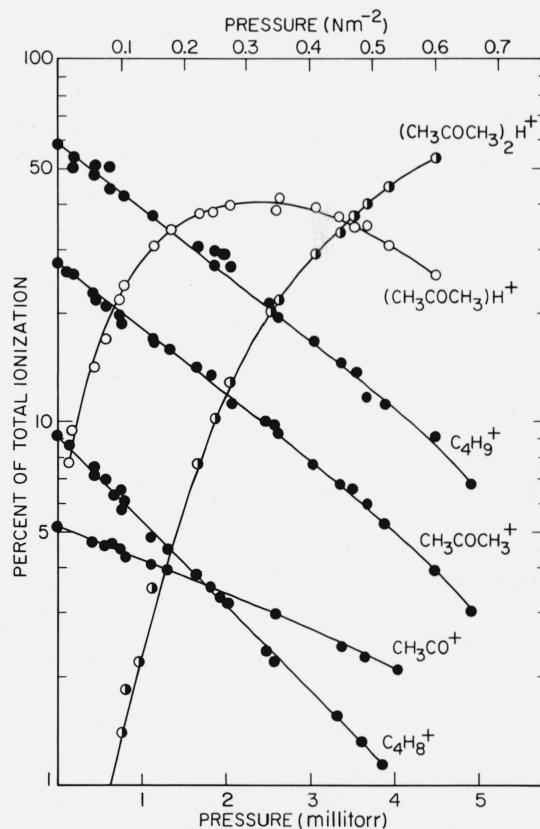


FIGURE 2. Photoionization of a 1:1 mixture of neopentane and acetone at 106.7–104.8 nm.

Composite mass spectrum as a function of chamber pressure for major ions.

region of low chamber pressures where the semi-logarithmic decay plot is linear. The downward curvature of the semilog decay for m/e 58, 57, etc., at higher pressures is due to an increase in the ionic residence time due to nonreactive scattering. Experiments with mixtures of various compositions yielded an average thermal bimolecular rate coefficient of $1.1 \pm 0.1 \times 10^{-9}$ cm³/molecule · second for the proton transfer reaction involving $t\text{-C}_4\text{H}_9^+$ and acetone. Proton transfer from $i\text{-C}_4\text{H}_8^+$ was found to be slightly more efficient. A thermal rate coefficient of $1.3 \pm 0.1 \times 10^{-9}$ cm³/molecule · second was derived for this process.

(h) Ammonia and methylamines—Process 3 was also found to occur efficiently in neopentane-NH₃ mixtures, as well as mixtures with methyl-, dimethyl- and trimethylamine. The thermal rate coefficients derived for these systems are given in table 1.

Additional experiments were carried out with neopentane- d_{12} , which yields 85.7 percent $t\text{-C}_4\text{D}_9^+$ and 14.3 percent C_4D_8^+ at the argon resonance lines. In mixtures of neopentane- d_{12} with trace amounts of NH₃ it was determined that the reaction $t\text{-C}_4\text{D}_9^+ + \text{NH}_3 \rightarrow$ products yields 3.6 percent NH₂D₂⁺ and 96.4 percent NH₃D⁺ as products, indicating that hydrogen exchange within the collision complex is a relatively inefficient process. No exchange was detected in any other reaction pairs except $t\text{-C}_4\text{D}_9^+ - \text{CH}_3\text{NH}_2$, which yielded approximately 2 percent (CND₂H₄)⁺. Trace amounts of the additives were used in order to minimize the probability for successive exchange reactions such as $\text{NH}_2\text{D}_2^+ + \text{NH}_3 \rightarrow \text{NH}_3\text{D}^+ + \text{NH}_2\text{D}$ which appear to remove the deuterium content of the primary reaction product.

Supplementary experiments involving acetone-NH₃ mixtures were also performed. These will be discussed in the appropriate portion of the text.

3. Discussion

3.1. Magnitude of the Rate Constant for Proton Transfer

The total rate constant for collision involving $t\text{-C}_4\text{H}_9^+$ ions and polar molecules may be approximated by assuming that the collision is described by a cross section for both ion-induced dipole [18] and ion-dipole interactions [19]. Calculated values for the ion dipole (k_μ) and ion-induced dipole (k_a) rate coefficients are included in table 1 for those reaction pairs in which proton transfer was found to occur. Within the limits of experimental error, the calculated values for k_a are in excellent agreement with the thermal macroscopic rate coefficients found in the present study. Although this agreement may be fortuitous, this equivalence suggests that ion-dipole interactions have little, if any, effect on the total cross section for collision if proton transfer occurs with unit efficiency (at every collision). The fact that very little hydrogen exchange occurs in the $t\text{-C}_4\text{H}_9^+ - \text{NH}_3$ and $t\text{-C}_4\text{H}_9^+ - \text{CH}_3\text{NH}_2$ reaction pairs, and none in the other systems, is a further indication

that the particle transfer occurs over a relatively large distance and within a "loose" ion-molecule complex.

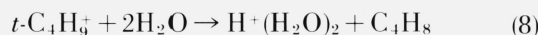
3.2. Thermochemical Considerations and Proton Affinities

The proton affinity (P.A.) of a molecule (M), which is defined as the negative of the enthalpy change associated with the reaction

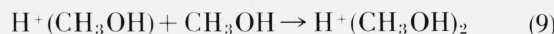


may be calculated provided that $\Delta H_f(\text{MH}^+)$ is known. Recently Lossing and Semeluk [20], using a refined energy resolved electron beam mass spectrometer, have determined the ΔH_f for the various isomeric butyl ions. Their value for $\Delta H_f(t\text{-C}_4\text{H}_9^+)$ of 167 kcal/mol (698 kJ/mol) yields a P.A. for $i\text{-C}_4\text{H}_8$ of 195 kcal/mol (815 kJ/mol) using Reaction 7. In order for proton transfer to occur from $t\text{-C}_4\text{H}_9^+$ to any of the molecules (X) investigated in this study, the P.A. (X) must be \geq P.A. ($i\text{-C}_4\text{H}_8$). Experimentally, $t\text{-C}_4\text{H}_9^+$ is found to transfer a proton to acetone but not to isopropanol. Since the value of Semeluk and Lossing for $\Delta H_f(t\text{-C}_4\text{H}_9^+)$ appears to have been determined very accurately, the P.A. of isopropanol must be \leq 195 kcal/mol unless the proton transfer reaction involving $t\text{-C}_4\text{H}_9^+$ is exothermic and exhibits an extremely high activation energy, which we feel is unlikely. On this basis, the value for the P.A. of isopropanol of 193 kcal/mol (807 kJ/mol) quoted by Beauchamp [14] seems reasonable.

Under results we pointed out that the termolecular proton transfer reaction



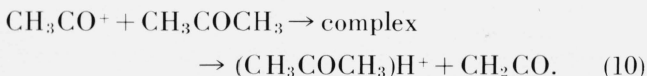
was not observed within our sensitivity limits, although reactions of this type have been observed previously for a variety of alkane and cycloalkane molecular ions [12c]. Based on the value of 36 kcal/mol (150 kJ/mol) [21] for the overall exothermicity of the solvation reaction process $\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}^+(\text{H}_2\text{O})_2$ and an average value for the $\Delta H_f(\text{H}_3\text{O}^+)$ of 145 ± 5 kcal/mol (606 ± 21 kJ/mol) derived from various sources, Reaction 8 would be approximately 4 kcal/mol (16 kJ/mol) exothermic taking the value for $\Delta H_f(t\text{-C}_4\text{H}_9^+)$ given by Lossing and Semeluk. However, the apparent exothermicity is equivalent in magnitude to the error limits associated with $\Delta H_f(\text{H}_3\text{O}^+)$; consequently the negative experimental result and the apparent exothermicity are not necessarily contradictory, particularly if the overall reaction is essentially thermoneutral. We cannot comment on Reaction 4, since the overall enthalpy change associated with the solvation process



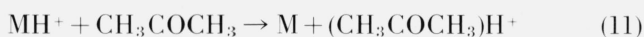
is unknown.

Since proton transfer occurs from $t\text{-C}_4\text{H}_9^+$ to acetone it is apparent that the P.A. (acetone) > P.A. (isobutene);

e.g., P.A. (acetone ≥ 195 kcal/mol (815 kJ/mol). In agreement with previous investigators [22, 23], we also find that the CH_3CO^+ fragment ion from acetone participates in a bimolecular reaction with acetone which is empirically equivalent to proton transfer



Assuming ground state reactants, and taking $\Delta H_f(\text{CH}_3\text{CO}^+)$ as 152 ± 2 kcal/mol (635 kJ/mol) and $\Delta H_f(\text{CH}_2\text{CO})$ as 11.4 kcal/mol (47.7 kJ/mol) [24], it is easily shown that P.A. (acetone) is $\geq 203 \pm 2$ kcal/mol (849 ± 8 kJ/mol). An upper limit for the P.A. (acetone) may be estimated either by determining (i) whether or not $(\text{CH}_3\text{COCH}_3)\text{H}^+$ will transfer a proton to a molecule (M) which has a known (and presumably higher) P.A. than acetone or (ii) by determining that the reaction



does not occur, and is therefore presumably endothermic. This combined method has been used successfully by Munson [16] to establish the relative vapor phase basicities for a variety of polar molecules. We have used the second alternative mentioned above to estimate an upper limit for the P.A. of acetone since we found it difficult to generate large yields of $(\text{CH}_3\text{COCH}_3)\text{H}^+$ by any suitable combinations of reactants and additives. Our approach was to establish whether or not NH_4^+ would participate in a proton transfer reaction with acetone. The most recent estimate of the P.A. of NH_3 is 207 kcal/mol (865 kJ/mol) [12b], which is very close to the lower limit for acetone derived above. The results of a typical experiment in which NH_3 - CH_3COCH_3 mixtures were photolyzed at 106.7–104.8 nm are shown in figure 3. It is apparent that the major initial reaction involving the primary ions $\text{CH}_3\text{COCH}_3^+$ and NH_3^+ is proton transfer to NH_3 to yield NH_4^+ . As the total pressure is increased, NH_4^+ is found to react with CH_3COCH_3 only via condensation:



The small yield of $(\text{CH}_3\text{COCH}_3)\text{H}^+$ which is observed is consistent with that expected from the interaction of $\text{CH}_3\text{COCH}_3^+$ and CH_3CO^+ with the acetone component in the mixture. The solvation of NH_4^+ by NH_3 to form $(\text{NH}_3)_2\text{H}^+$ is also observed, as well as the further solvation of $(\text{CH}_3\text{COCH}_3)\text{NH}_4^+$ and $(\text{NH}_3)_2\text{H}^+$ by acetone:

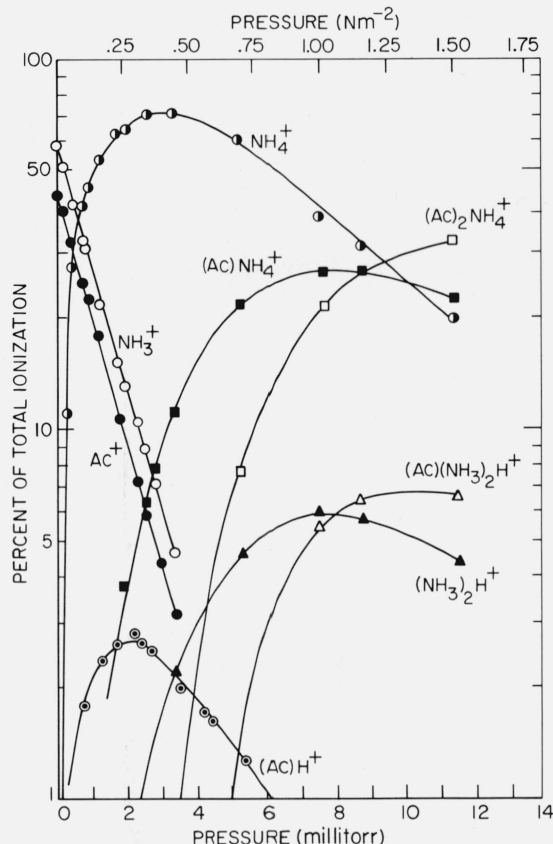
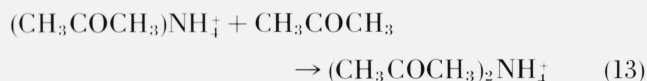


FIGURE 3. Photoionization of a mixture containing 83 percent ammonia and 17 percent acetone at 106.7–104.8 nm as a function of total pressure.

AC = Acetone.

No evidence was found for the reaction



in any of the mixtures investigated. Based on the assumption that Reaction 15 would have occurred if exothermic, which appears to be valid for this class of reactions according to Munson's results, we conclude that $\text{P.A.}(\text{NH}_3) > \text{P.A.}(\text{acetone})$, or that 203 ± 2 kcal/mol $< \text{P.A.}(\text{acetone}) < 207$ kcal/mol.

3.3. Absolute Rates for Process 1

As stated in the Introduction, one of the objectives of this study was to provide a basis for converting the relative rate constants for Process 1, which were previously measured in this laboratory [1], to absolute values. Our experimental value for Reaction 2 is lower than the value assumed in that study by a factor of approximately 4.4, and the reported values should be adjusted accordingly. The fact that the rate coefficients for Process 1 are significantly lower than even originally thought adds further credence to the conclusions of Ausloos and Lias [1] that the rates of the hydride transfer process involving $t\text{-C}_4\text{H}_9^+$ and higher hydro-

carbons are influenced by the combined effects of activation energy and steric hinderance.

We are indebted to P. Ausloos for his encouragement and counsel during the course of this study.

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